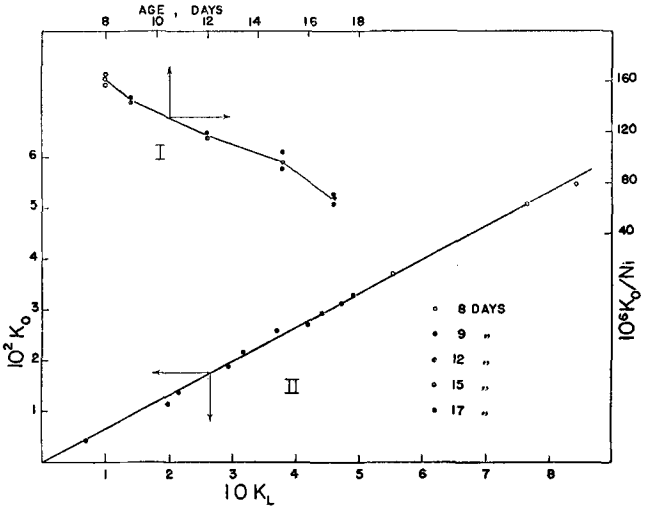

FIG. 2. Plot I. Decline of catalytical activity k_0/Ni on aging. Plot II. Constancy of selectivity index k_L/k_0.

k_L/k_0 can be obtained within an hour at little expense of work or material.

The above results do not give any clue as to what alternative route the reaction is taking or whether the two routes are followed simultaneously at an equal rate. A chromatographic study of oxidative material (point D on the absorption curve, Figure 1) gives the answer to this problem. It will be published at a later date.

REFERENCES

1. Adkins, H., and Billica, H. R., J. Am. Chem. Soc., *70*, 695 (1948).
2. Bailey, A. E., J. Am. Oil Chemists' Soc., *26*, 644 (1949).
3. Brice, B. A., and Swain, M. L., J. Opt. Soc. Am., *35*, 532 (1945).
4. Mattil, K. F., and Longenecker, H. E., Oil and Soap, *21*, 16 (1944).
5. Riemenschneider, R. W., Herb, S. F., and Nichols, P. L., J. Am. Oil Chemists' Soc., *26*, 371 (1949).
6. Swift, C. E., Rose, W. G., and Jamieson, G. S., Oil and Soap, *20*, 249 (1943).
7. Vandenheuvel, F. A., J. Am. Oil Chemists' Soc., *33*, 347 (1956).
8. Vandenheuvel, F. A., Anal. Chem., *24*, 847 (1952).

[Received January 18, 1956]

The Migration of Double Bonds During the Isomerization of Methyl Linoleate with Palladium on Carbon Catalyst

K. H. TAKEMURA and L. A. GOLDBLATT, Southern Regional Research Laboratory,[1] New Orleans, Louisiana

IN CONNECTION with work being carried out in this laboratory on increasing the chemical utility of linoleic acid, a component of cottonseed oil and foots, the catalytic isomerization of the acid to conjugated forms was investigated. Studies on the isomerization of vegetable oils containing linoleic acid have been summarized by Narayan and Kulkarni (8). Radlove *et al.* (10) obtained 30–40% conjugation on treatment of vegetable oils with a nickel-carbon catalyst. Methyl linoleate was reported to give approximately 60% diene conjugation with this catalyst.

In the present work the isomerization of methyl linoleate was studied, using palladium on carbon as catalyst. Moore (7) has studied the formation of "iso-oleic" acids during the hydrogenation of the oleic acid with palladium catalyst. There is mention by Radlove *et al.* (10) of palladium as an isomerization catalyst, and they state "preliminary experiments disclosed that a small amount of conjugation could be achieved by heating either vegetable oils or their methyl esters with platinum, palladium, and nickel catalysts." The Naval Stores industry makes extensive use of palladium-carbon catalysts for the isomerization and disproportionation of rosin (4), but no details concerning the experiments with palladium are given. A survey of the literature yielded no previous report on the use of palladium on carbon as a catalyst for the isomerization of vegetable oils or linoleates. After this work was completed, Floyd, Baldwin, Paschke, and Wheeler reported fairly extensive aromatization and hydrogenation of methyl linoleate by treatment with palladium on carbon catalyst at 275°C. (3a).

In the course of this work it became of interest to determine the location of the double bonds in the isomerized methyl linoleate. The isomerized ester was therefore oxidatively cleaved, and the acids produced were identified by partition chromatography. Studies of this type had been made previously (1, 2) in connection with the migration of double bonds during the partial hydrogenation of esters of oleic elaidic, petroselinic, and linoleic acid.

[1] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

Experimental

Methyl linoleate was prepared by esterification of linoleic acid obtained from saponification of safflower oil and urea complexing, essentially according to the method of Swern *et al.* (12). Two batches of distilled methyl linoleate were used: one with N_D^{26} 1.4585, iodine-value (Wijs) 163.6 of about 90% purity, and the other distilling at 142 to 146°C. at 0.2 to 0.3 mm., N_D^{27} 1.4590, iodine-value 170.9 of approximately 99% purity.

Isomerization

The ester was heated with stirring under nitrogen at temperatures ranging from 150–250 ± 5°C. in the presence of 2–25% by weight of 10% palladium on carbon (Baker and Company, Newark, N. J., Activity 950, Lot No. 1489).[2] Samples of the reaction mixture were taken at intervals and measured spectrophotometrically for percentage of conjugation.

Hydrogen-iodine values on certain samples were determined by the method described by Pack *et al.* (9).

Oxidation

The distilled, isomerized ester was saponified with dilute (0.25 *N*) alcoholic potassium hydroxide. The acid was then oxidized with ozone by a method similar to that described by R. R. Allen.[3]

[2] It is not the policy of the Department of Agriculture to recommend commercial firms or their products. The name given above is merely for your information and convenience.

[3] Private communication.

One-half gram of the acid dissolved in 50 ml. of acetone (C.P.) was treated with twice the theoretical amount of ozone (approximately 1 hr.) with cooling in an ice-salt bath. Ten milliliters of water were then added, and the solution was refluxed for 1 hr. The solution was cooled and again treated with ozone for about 15 min. The resultant solution was neutralized with dilute aqueous sodium hydroxide and evaporated to dryness. The oxidation mixture was made neutral to avoid loss of volatile monobasic acids during the evaporation.

Chromatography

The acids obtained by oxidation were analyzed by partition chromatography. The columns were prepared, using silicic acid, 100-mesh, Mallinckrodt Analytical Reagent suitable for chromatographic analysis.[2] The separation of monobasic acids (C_4 and higher) from the higher dibasic acids (C_6–C_{13}) was accomplished by the method of Marvel and Rands (6).

A sample of the acids was prepared for chromatography by mixing 50–70 mg. of the sodium salts from the oxidation with 0.5–1 g. of silicic acid and acidifying with about 0.5 ml. of 2 *N* sulfuric acid. Samples for succeeding chromatographic separations were prepared in a similar manner except for changes in the acidifying agent, as indicated below. The sample so prepared was then added to the column. The eluate fractions (titrated) containing salts of monobasic acids were combined and evaporated to dryness. The salts of the dibasic acids were isolated in a similar fashion by combining and evaporating the appropriate fractions.

The monobasic acids were separated by the procedure of Ramsey and Patterson (11), using iso-octane as the eluant. The sample used was acidified with a methanol solution of citric acid.

The method of Higuchi *et al.* (5) with some modifications was used for the separation of dicarboxylic acids. It was found that the use of 18.75 ml. instead of 25 ml. of citrate buffer (pH 5.4) per 25 g. of silicic acid made the packing of the column much simpler and eliminated the necessity of using a plunger to pack the silicic acid. No adverse effect upon the separation of the acids was found by this change in the amount of buffer used.[4] In eluting the acids, 100 ml. of each of the following solutions of butanol in chloroform were used: 3%, 5%, 10%, 15%, 20%, 25%, and 30%. The presence of any short chain monobasic acids (C_2–C_3) was found to interfere in this chromatographic separation. To insure their absence the sodium salts of the dibasic acids were acidified with dilute aqueous hydrochloric acid. The resultant mixture was evaporated to dryness on a steam bath and then finally converted back to sodium salts. The chromatographic sample was then acidified with aqueous citric acid before placing it on the column.

The fractions containing the C_{10} dicarboxylic acid thus obtained were found to contain higher dicarboxylic acids. These were therefore combined, evaporated to dryness, and re-chromatographed. The column used for this separation was prepared with 2 M. glycine buffer (pH 8.5) (3). The acids were eluted with 70 ml. of chloroform and then with 70 ml. each of 1.5%, 5%, 10%, and 20% butanol in chloroform. Aqueous citric acid was used to acidify the sample.

[4] E. R. Cousins and W. A. Guice, this laboratory, private communication.

Results and Discussion

Heating methyl linoleate with palladium on carbon resulted in an initial rapid rise in conjugation, which soon reached a maximum and then gradually decreased (Figures 1–3). The maximum conjugation of methyl linoleate, 24%, was obtained after 4 hrs. at 200 ± 5°C. with 25% by weight of catalyst. The gradual decrease in conjugation as heating is continued beyond the time of maximum conjugation is probably caused by isomerization as well as dimerization or polymerization of the conjugated material. It is quite probable that some conjugated ester is formed during this period of decrease, but the amount must be small.

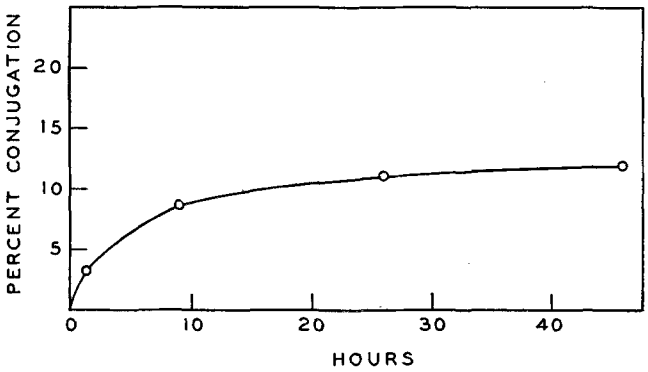

FIG. 1. Isomerization of methyl linoleate—150 ± 5°C. 10% catalyst.

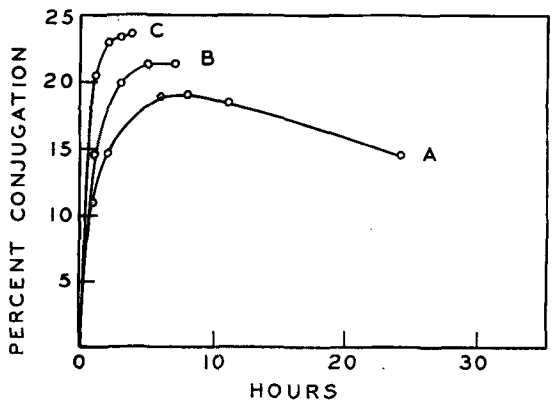

FIG. 2. Isomerization of methyl linoleate—200 ± 5°C.
A— 4% catalyst.
B—10% catalyst.
C—25% catalyst.

The final reaction mixtures from two reactions (Figures 2-A and 3-A) were distilled. Yields of 85% and 94%, respectively, of monomeric products boiling at 125–140°C./0.12–0.15 mm. were obtained. The high yields of distillate indicated that the degree of conjugation attained is not limited entirely by dimerization or polymerization of conjugated product. It seems more probable that the double bonds are migrating in a random manner, some shifting towards

TABLE I

Migration of the Double Bonds of Methyl Linoleate During Isomerization with Palladium on Carbon Catalyst
(Temperature, 200 ± 5°C.; 5% of 10% Pd/C by weight)

Sample No.	Reaction time	Distillation temperature	Pressure	Yield	Refractive index 25°C.	% Conjugation	Hydrogen iodine value [a]	Composition of long chain dicarboxylic acids from ozonization, mole %							
								C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}[b]
1	0.5 hr.	120–123°C.	0.1 mm.	95%	1.4613	11.4	170	—	7	10	60	12	2	1.5	7
2	22 hrs.	118–120°C.	0.1 mm.	95%	1.4634	21.0	133	0.3	12	13	39	13	7	6	9
3	46 hrs.	118–120°C.	0.1 mm.	70%	1.4660	15.8	120	0.5	7	14	33	12	11	8	13

[a] Theoretical value for methyl linoleate used: 170.
[b] Includes higher unidentified acids.

one another and giving rise to conjugated dienes, and others moving away to structures wherein the olefinic bonds are further apart. Indeed chromatographic studies of the acids obtained from the oxidative cleavage of isomerized methyl linoleate substantiated this. Ultraviolet absorption spectra did not indicate the presence of any cyclized, aromatic components even after 46 hrs. of heating at 200°C. but showed the formation of aromatics at 250°C.

Results of chromatographic work are summarized in Table I. The origin of the C_{12} and C_{13} dicarboxylic acids (and probably part of the C_{11}) is presumed to be a result of partial hydrogenation of the olefinic bond closer to the carboxyl group. The activity of Pd/C as a hydrogenation-dehydrogenation catalyst introduces to these experiments some resemblance to the partial hydrogenation work of previous investigators. It is therefore not surprising that the dicarboxylic acids found here are, in general, those previously reported.

The analysis of monobasic acids obtained from the oxidation of isomerized linoleate was incomplete. Only two monobasic acids were identified, caproic (C_6) and heptylic (C_7).

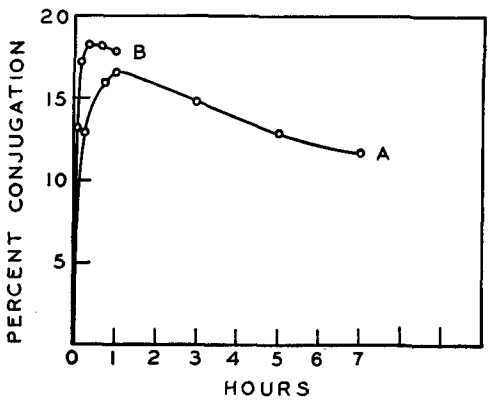

FIG. 3. Isomerization of methyl linoleate—250 ± 5°C.
A— 4% catalyst.
B— 10% catalyst.

Summary

The isomerization of methyl linoleate by heating with palladium on carbon catalyst gave an initial rapid rise in the degree of conjugation which reached a maximum and then gradually decreased. The maximum conjugation obtained was about 24% after 4 hrs. of heating at 200 ± 5°C. with 25% by weight of catalyst. Ultraviolet absorption spectra did not indicate the presence of any cyclized aromatic components even after 46 hrs. of heating at 200°C. but showed the formation of aromatics at 250°C. The limit of conjugation obtained is a result of random migration of the olefinic bonds rather than dimerization or polymerization reactions.

Acknowledgments

The authors wish to thank E. R. Cousins and Wilma A. Guice for their advice and assistance in connection with the chromatographic analysis. They also wish to thank R. T. O'Connor and Dorothy C. Heinzelman for the spectrophotometric work in the isomerization studies.

REFERENCES

1. Allen, R. R., and Kiess, A. A., J. Am. Oil Chemists' Soc., *32*, 400–5 (1955); and Allen, R. R., and Kiess, A. A., abstracts of papers presented at American Oil Chemists' Society meeting, Minneapolis, October 1954.
2. Boelhouwer, C., Gerckens, J., Lie, O. T., and Waterman, H. I., J. Am. Oil Chemists' Soc., *30*, 59–61 (1953).
3. Corcoran, G. B., Anal. Chem., *28*, 168 (1956).
3a. Floyd, D. E., Baldwin, W. S., Paschke, R. F., and Wheeler, D. H., abstracts of papers presented at American Oil Chemists' Society meeting, Houston, April 1956.
4. Hays, J. T., Drake, A. E., and Pratt, Y. T., Ind. Eng. Chem., *39*, 1129–32 (1947).
5. Higuchi, T., Hill, N. C., and Corcoran, G. B., Anal. Chem., *24*, 491–3 (1952).
6. Marvel, C. S., and Rands, R. D., J. Am. Chem. Soc., *72*, 2642–6 (1950).
7. Moore, C. W., J. Soc. Chem. Ind., *38*, 320–5 T (1919).
8. Narayan, K. A., and Kulkarni, B. S., Paintindia, *2*, No. 5, 15–18 (1952).
9. Pack, F. C., Planck, R. W., and Dollear, F. G., J. Am. Oil Chemists' Soc., *29*, 227–8 (1952).
10. Radlove, S. B., Teeter, H. M., Bond, W. H., Cowan, J. C., and Kass, J. P., Ind. Eng. Chem., *38*, 997–1002 (1946).
11. Ramsey, L. L., and Patterson, W. I., J. Asso. Off. Agr. Chem., *31*, 139–150 (1948).
12. Swern, Daniel, and Parker, W. E., J. Am. Oil Chemists' Soc., *30*, 5–7 (1953).

[Received July 12, 1956]

Conductivity Method for the Control of a Soap Dryer

L. J. OKHOLM, F.D.B.'s Soap Factories, Viby J., Denmark

THE USUAL LABORATORY METHODS for determining fatty acid contents of dried soaps containing 80 to 85% fatty acids are too time-consuming for adequate automatic control of the drying process. However a method based on the measurement of the electrical conductivity of compressed soap makes possible effective control of the soap-drying process.

Soap entering the vacuum dryer has a fatty acid content of 62 to 65%. Depending on end-use, such as soap flakes or toilet soap, the fatty acid content of the soap base is specified as minimum 80.0, 82.0%,